UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
NATIONAL EXPOSURE RESEARCH LABORATORY
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OFFICE OF
RESEARCH AND DEVELOPMENT

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Subject: NJ DEP Report #2: Non-targeted Analysis Results of PFAS in Soil and Vegetation

Dear Mr. Kloo:

I am pleased to provide you with the laboratory report of non-targeted analysis results identifying the occurrence of chloro-perfluoro-polyether-carboxylate (ClPFPECA) concentrations in soils and vegetation. This is the second in a series of reports prepared as a part of EPA Office of Research and Development's (ORD) collaboration with the New Jersey Department of Environmental Protection (NJ DEP) and EPA Region 2 on the study, "Detection, Evaluation, and Assignment of Multiple Poly- and Perfluoroalkyl Substances (PFAS) in Environmental Media from an Industrialized Area of New Jersey." This report includes concentration results for PFAS in 24 soil and 24 vegetation samples. The ORD Principal Investigators (PIs) for this study are Drs. Andy Lindstrom, Mark Strynar, and John Washington. The results in this report were generated by Dr. John Washington in our Athens, Georgia laboratory. It is my understanding that these samples were collected by NJ DEP November 8 - 10, 2017 from various locations in the vicinity of the Solvay and Dupont facilities.

We do not interpret exposure or risk from the values presented in this report. EPA does not currently have health-based standards, toxicity factors, or associated risk levels for per- or poly-fluorinated alkyl substances (PFAS), other than perfluorooctanoic acid (PFOA) and perfluorocatane sulfonate (PFOS). While the data provided indicate the presence of certain PFAS in soil samples, it does not offer interpretation as to human or environmental exposure or risk.

Thank you for providing us with this opportunity for collaboration that helps to further both EPA's and New Jersey's understanding of an important public health issue. If you have any questions or concerns about this report, do not hesitate to contact me at (919) 541-2107 or via email at watkins.tim@epa.gov or Tim Buckley at (919) 541-2454 or via email at buckley.timothy@epa.gov. I look forward to our continued work together.

Sincerely,

Timothy H. Watkins
Director
National Exposure Research Laboratory
Office of Research and Development

Enclosure

CC:

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Detection, Evaluation, and Assignment of PFAS in Environmental Media from an Industrialized Area of New Jersey

Laboratory Data Report #2: Non-targeted Analysis of PFAS in Soil and Vegetation

Background. This report stems from a collaborative study with EPA ORD, EPA Region 2, and NJ DEP entitled "Detection, Evaluation, and Assignment of Multiple Poly- and Perfluoroalkyl Substances (PFAS) in Environmental Media from an Industrialized Area of New Jersey." NJ DEP assumed responsibility for the collection of samples and their shipment to the ORD laboratory. ORD was responsible for sample extraction and analysis of PFAS. ORD's analysis and support team that contributed to this effort are listed in Table 1.

Table 1. EPA Office of Research and Development analysis and report team.

Responsibility	Personnel
ORD Principal Investigators	Andy Lindstrom, Mark Strynar, John Washington
Laboratory chemistry	John Washington (PI), Tom Jenkins
Quality Assurance Review	Brittany Stuart
Management coordination and review	Brian Schumacher, Tim Buckley
Report Preparation	Kate Sullivan, Tim Buckley

This 2nd report includes non-targeted analysis results of 24 soil samples and 4 quality control (QC) samples labeled with "PFSS" as well as 24 vegetation samples labeled with "PFVG" that were collected by NJ DEP on November 8-10, 2017. Samples were sent to and analyzed for PFAS under the direction of Dr. John Washington at ORD's laboratory in Athens, GA. Samples were received on November 14, 2017.

The current data report is intended to provide a simple representation and summary of the analysis results. Therefore, the description of methods and quality assurance are brief and high-level. Additional reports and/or publications are being developed that will include a more detailed description of methods, quality assurance procedures, and statistical/geospatial interpretation of the data. As study partners/collaborators, we anticipate that NJ DEP will assist in these reports and publications.

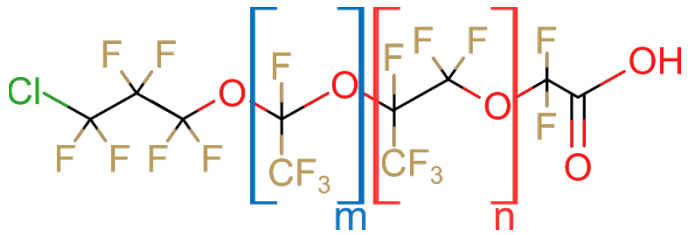
Methods in Brief. The PFAS reported here were extracted and analyzed according to methods documented within an approved Quality Assurance Project Plan (QAPP).[1] PFAS were identified and quantified using a non-targeted analysis approach. The non-targeted analysis differs from targeted analysis in that chemical identification and quantification does not have the benefit of being based on a known standard for each compound. Accordingly, there is more uncertainty both in terms of identification and concentration estimation for these non-targeted analytes.

[1] [1]National Exposure Research Laboratory, Quality Assurance Project Plan: Detection, Evaluation and Assignment of Multiple Poly and Per-fluoroalkyl Substances (PFAS) in environmental media from an industrialized area of New Jersey. Prepared for New Jersey Department of Environmental Protection (NJ DEP), September 14, 2017.

Samples were extracted with 90%/10% acetonitrile/water followed by a liquid/liquid cleanup. Samples were first analyzed for nontargeted novel PFAS by liquid chromatography/mass spectrometry using a Waters Acquity UPLC coupled to a Waters Xevo quadrupole time-of-flight (QToF) mass spectrometer to tentatively identify novel PFAS and to elucidate their fragmentation. PFAS compounds were then semi-quantitated on a Waters Acquity UPLC coupled to a Waters Quattro Premier tandem mass spectrometer (MS/MS) based on criteria including: i) internal consistence among samples for elution time, ii) molecular-precursor mass, iii) molecular-fragment mass, iv) signal-to-noise contrast, and v) temporal continuity of signal. Detection of a congener within a sample was determined based on criteria of signal-to-noise contrast and temporal continuity of signal. Concentrations of the PFAS analytes were semi-quantified on the MS/MS using the ratio of the analyte peak area to the peak area of an internal standard ($^{13}C_5$-labeled perfluorononanoic acid, M5PFNA) added to all samples at a precisely known concentration. The quantification of the non-targeted analyte assumes that the mass spectrometer responds to M5PFNA as it does the reported analytes, i.e. yielding identical chromatographic peak areas for a given concentration. Our experience with PFAS suggests that this means of estimation is within an order of magnitude of the actual concentration. Even though the absolute concentration estimate will be uncertain, relative comparisons between samples for a given congener will be much less so.

Summary of Results. Here, we tentatively identified the presence of nine novel PFAS in soil and plant samples. The nine PFAS are congeners of chloro-perfluoro-polyether-carboxylate (ClPFPECA). Their generic structure is shown in Figure 1 and their mass spectral features are provided in Table 2. Based on the prevalence of these congeners associated with Solvay, we have high confidence in these chemical identifications. This identification is also consistent with measurements by Wang et al. 2018.[2]

Figure 1. Generic Structure of Chloro-Perfluoro-Polyether-Carboxylate (ClPFPECA). There are nine congeners with m and n varying from 0-3.



The MS/MS features of ClPFPECA congeners identified in soils and plants using non-targeted analysis are presented in Table 2. For these analyses, there was no indication of laboratory contamination as ClPFPECA was not detected in any process blanks (n=6) or field blanks (soil only n=2).

[2] Wang Y, Yu N, Zhu X, Guo H, Jiang J, Wang X, Shi W, Wu J, Yu H, Wei S. Suspect and Nontarget Screening of Per- and Polyfluoroalkyl Substances in Wastewater from a Fluorochemical Manufacturing Park. Environ Sci Technol. 2018 Oct 2;52(19):11007-11016. doi: 10.1021/acs.est.8b03030. Epub 2018 Sep 24. PubMed PMID: 30211545 .

Table 2. MS/MS Features of Chloro-Perfluoro-Polyether-Carboxylate (ClPFPECA) Congeners Identified in Soils and Plants Using Non-Targeted Analysis.

Carbon Chain Length	Anion Formula	Number of Ethyl, Propyl Groups	Molecular Mass (g/mol)	Precursor	Fragment	Elution Time (m) Soils (Plants)
7	$C_7ClF_{12}O_4$	1,0	410.9294	316.9447	200.9542	2.3 (2.3)
8	$C_8ClF_{14}O_4$	0,1	460.9262	366.9395	200.9542	2.6 (2.6)
9	$C_9ClF_{16}O_5$	2,0	526.9179	432.9312	200.9542	3.4 (3.4)
10	$C_{10}ClF_{18}O_5$	1,1	576.9147	482.9280	200.9542	3.9 (3.9)
11	$C_{11}ClF_{20}O_5$	0,2	626.9115	532.9249	200.9542	4.6 (4.23)
11	$C_{11}ClF_{20}O_6$	3,0	642.9064	548.9198	200.9542	4.9 (4.47)
12	$C_{12}ClF_{22}O_6$	2,1	692.9032	598.9166	200.9542	5.5 (5.25)
13	$C_{13}ClF_{24}O_6$	1,2	742.9000	648.9134	200.9542	6.1 (6.1)
14	$C_{14}ClF_{26}O_6$	0,3	792.8968	698.9102	532.9249	6.7 (6.4)

Semi-quantitative concentration estimates of PFAS congeners are given by sample IDs assigned by NJ DEP for 24 soil samples and 4 QC samples in Table 3. A summary of observations for soil sample results include:

- 9 PFAS congeners were found at measurable concentrations in at least one soil sample with 3 congeners detected in all 24 of the samples (C8, C10, C11(0,2)).
- Soil concentrations of C8, C10, and C11(0,2) were relatively high in most samples. The maximum PFAS concentration in soil was 1,580 pg/g for C10 for sample ID PFSS008.
- Congeners C7, C13, and C14 were either not detected or found at low concentrations at most sites.

Table 4 shows semi-quantitative concentration estimates of PFAS congeners for 24 vegetation (plant) samples. A summary of observations for vegetation sample results include:

- 9 PFAS congeners were found at measurable concentrations in at least one of the vegetation samples with 3 congeners detected in measurable concentrations in most of the vegetation samples (C8, C10, C11(0,2)).
- Vegetation concentrations of C8, C10, and C11(0,2) were relatively high in most samples. The maximum PFAS concentration in vegetation was 14,500 pg/g for C8 for sample ID PFVG008.
- Congeners C7, C9, and C11(3,0) to C14 were either not detected or found at low concentrations in most of the vegetation samples.

Overall summary for both soil and vegetation results:

- C8, C10, and C11(0,2) congeners were found in relatively high concentrations in both soil and vegetation at most sites. Concentrations were consistently greater in vegetation than soils, with a maximum ratio $\frac{Veg}{Soil}$ for C8 of 40.7 observed at site "008". This is partly related to reporting of concentrations on a dry-mass basis, owing to the relatively greater loss of moisture mass for the vegetative samples relative to soil.

Table 3. Semi-Quantitative Concentrations of Chloro-Perfluoro-Polyether-Carboxylate (ClPFPECA) Congeners in Soil Samples Determined with Non-targeted Analysis Expressed in pg/g.

Carbon Length	*C7*	*C8*	*C9*	*C10*	*C11*	*C11*	*C12*	*C13*	*C14*
Formula	$C_7ClF_{12}O_4$	$C_8ClF_{14}O_4$	$C_9ClF_{16}O_5$	$C_{10}ClF_{18}O_5$	$C_{11}ClF_{20}O_5$	$C_{11}ClF_{20}O_6$	$C_{12}ClF_{22}O_6$	$C_{13}ClF_{24}O_6$	$C_{14}ClF_{26}O_6$
Ethyl, Propyl Groups	**1,0**	**0,1**	**2,0**	**1,1**	**0,2**	**3,0**	**2,1**	**1,2**	**0,3**
Soil Sample ID	**Soil Concentrations as M5PFNA (by simple ratios to matrix internal standard in pg/g soil)**								
PFSS001	3.0	703	13.9	1,350	509	35.4	108	9.1	31.5 (JP)
PFSS002	ND	63.5	1.4	154	57.4	3.7	11.8	1.4	3.9
PFSS003	ND	61.2	1.3	85.7	42.3	3.9 (JP)	15.7	0.8	2.0 (JP)
PFSS004	13.9	293	3.9	330	89.0	5.4	12.3	1.3	2.3 (JP)
PFSS005	0.4	95.2	0.7	72.5	22.5	1.5	2.6	0.1	0.4
PFSS006	ND	68.5	1.1	87.7	29.1	0.8	4.4	ND	ND
PFSS007	0.5	75.8	0.7	31.7	8.4	0.7	1.1	ND	0.1
PFSS008	0.7	356	8.8	1,580	600	44.8	125	11.0	31.9
PFSS009	0.6	89.5	1.1	68.4	33.7	2.1	5.7	0.2 (JP)	1.3
PFSS010	ND	29.4	ND	34.7	18.2	0.8	4.3	ND	1.2
PFSS011	0.3	75.9	1.0	68.8	20.7	1.8	1.7	ND	0.3
PFSS012	ND	79.8	1.4	84.7	32.1	2.0	8.8	ND	ND
PFSS013	ND	45.0	ND	25.1	10.1	1.2	4.2	ND	0.3
PFSS014	ND	68.7	2.4 (JP)	92.1	42.9	1.7	7.1	0.6	0.8
PFSS015	1.2	74.3	1.4	91.5	26.1	1.3	3.4	ND	1.3
PFSS016	ND	33.3	0.9	12.1	2.7	ND	ND	ND	ND
PFSS017	ND	23.1	ND	15.3	9.2	ND	3.2	ND	ND
PFSS018	ND	14.5	0.3	19.1	8.4	ND	0.9	0.3	ND
PFSS019	ND	113	1.0	56.2	16.6	0.9	2.8	ND	0.3
PFSS020	ND	66.9	ND	76.3	28.1	1.4	5.4	ND	1.5 (JP)
PFSS021	ND	33.4	ND	33.4	11.5	ND	2.9	ND	0.4
PFSS022	ND	14.4	ND	10.1	4.6	ND	0.7	ND	ND
PFSS023	ND	83.6	1.7	99.5	24.0	ND	5.4	ND	1.1
PFSS024	ND	32.3	0.8	21.5	10.5	ND	3.2	ND	ND
PFSSDUP1	ND	55.3	ND	42.8	25.8	ND	ND	ND	ND
PFSSDUP3	ND	99.1	1.2	142	63.2	ND	3.4	ND	ND
PFSSFB1	ND	ND	ND	ND	ND	ND	ND	ND	ND
PFSSFB2	ND	ND	ND	ND	ND	ND	ND	ND	ND

ND: Non-detect based on criteria of signal-to-noise contrast and temporal continuity of signal.
JP: Result does not meet acceptance criteria for precision of >50% relative difference.

Table 4. Semi-Quantitative Concentrations of Chloro-Perfluoro-Polyether-Carboxylate (ClPFPECA) Congeners in Vegetation Samples Determined with Non-targeted Analysis Expressed in pg/g.

Carbon Length	*C7*	*C8*	*C9*	*C10*	*C11*	*C11*	*C12*	*C13*	*C14*
Formula	$C_7ClF_{12}O_4$	$C_8ClF_{14}O_4$	$C_9ClF_{16}O_5$	$C_{10}ClF_{18}O_5$	$C_{11}ClF_{20}O_5$	$C_{11}ClF_{20}O_6$	$C_{12}ClF_{22}O_6$	$C_{13}ClF_{24}O_6$	$C_{14}ClF_{26}O_6$
Ethyl, Propyl Groups	**1,0**	**0,1**	**2,0**	**1,1**	**0,2**	**3,0**	**2,1**	**1,2**	**0,3**
Vegetation Sample ID	**Vegetation Concentrations as M5PFNA (by simple ratios to matrix internal standard in pg/g dry plant)**								
PFVG001	ND	1,680	ND	856	371	15.8	49.3	ND	10.3
PFVG002	ND	269	ND	128	82.4	ND	10.6	ND	ND
PFVG003	ND	289	ND	475 (JP)	344	30.8	89.5	ND	5.9 (JP)
PFVG004	ND	1,010	80.1 (JP)	401	126	ND	ND	ND	ND
PFVG005	ND	1,880	ND	579	152	ND	ND	ND	ND
PFVG006	ND	333	ND	126	21.8	ND	ND	ND	ND
PFVG007	ND	116	ND	119	53.9	ND	ND	ND	ND
PFVG008	ND	14,500	80.0	9,750	3,100	222 (JP)	387 (JP)	30.0	87.2
PFVG009	ND	266	74.0 (JP)	1,010	173 (JP)	ND	42.4	ND	ND
PFVG010	ND	149	ND	259	44.7	ND	7.6	ND	ND
PFVG011	ND	261	ND	953	339	ND	ND	ND	ND
PFVG012	ND	161	ND	56.9	7.2	ND	ND	ND	ND
PFVG013	ND	470	ND	48.5	9.2	ND	ND	ND	ND
PFVG014	ND	945	ND	181	26.9	ND	119 (JP)	ND	2.1
PFVG015	ND	769	ND	452	60.5	ND	26.3	ND	2.0
PFVG016	ND	289	ND	44.1	9.0	ND	4.2	ND	ND
PFVG017	ND	150	ND	36.5	7.1	ND	6.4	ND	ND
PFVG018	ND	423	ND	ND	ND	ND	ND	ND	ND
PFVG019	ND	3,230	ND	381	51.7	ND	ND	ND	ND
PFVG020	ND	336	ND	325	49.2	7.1	14.8	ND	ND
PFVG021	4.1	33.6	ND	23.5	10.9	ND	ND	ND	ND
PFVG022	ND	ND	ND	ND	ND	ND	ND	ND	ND
PFVG023	ND	644	ND	304	73.5	ND	23.5	ND	ND
PFVG024	31.4	970	ND	32.8	7.9	ND	ND	ND	ND

ND: Non-detect based on criteria of signal-to-noise contrast and temporal continuity of signal.
JP: Result does not meet acceptance criteria for precision of >50% relative difference.